

September 1, 1967

Interim Report No. 1
SRI Project No. PAD-6146

JPL Contract No. 951522
Subcontract under NASA Contract NAS7-100
Task Order No. RD-29

EFFECT OF ENVIRONMENT ON THERMAL CONTROL COATINGS

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**This work was performed for the Jet Propulsion Laboratory,
California Institute of Technology, sponsored by the
National Aeronautics and Space Administration under
Contract NAS7-100.**

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N67-40089

FACILITY FORM 602	(ACCESSION NUMBER)	(THRU)
	25	
	(PAGES)	(CODE)
	01-89555	26
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

Copy No. 8

ABSTRACT

The use of additives to provide surface recombination centers on thermal control coatings, and thus to stop optical degradation, has been explored. Various chemical surface additives have been examined to test their electron and hole capture efficiency. Out of the group examined, iron was selected as the most promising. Preliminary tests of ZnO with this additive indicated no detectable damage when the ZnO was exposed to ultraviolet radiation under vacuum; permanent changes in resistance were used as the measure of damage. The required research to determine and test an optimized additive is discussed. Measurements to determine the degradation mechanism on additive-free ZnO are discussed and a theoretical model of degradation from ultraviolet radiation under vacuum is presented.

A. SUMMARY

Several chemicals that can provide surface recombination centers for ZnO have been tested for hole and electron reactivity, using the electrolytic method. These include ions of iron, arsenic, copper, manganese, chromium, tartarate, and iodine. The results are presented, together with a tentative theory to link the electron reactivity of the oxidized forms. From the theory and experiment, iron appears to be the most promising material of the group.

Methods for testing the recombination efficiency of additives in vacuum have been developed. It was originally proposed that gas evolution be measured both on single crystals and powders, and the evolution rate be taken as a measure of recombination efficiency. However, photolytic gas evolution was not detected on single crystals, so the approach was changed to conductance measurement (for single crystals) and ESR measurement (for powders). Changes in these measured quantities can be associated with degradation of the sample and also with surface recombination velocity. A preliminary examination of both these methods has been made on additive-free ZnO. A few measurements of ZnO with an iron additive for surface recombination centers has been made by the conductance (single crystal) method, and the additive appears to be quite effective.

A third area of interest in the program has been the study of the mechanism of coloration for additive-free ZnO. A model which fits present observations, based on dislocations, is discussed. The results of preliminary measurements of optical and electrical properties after coloration are compared with theoretical predictions of the dislocation model. However, the data are not precise enough for firm conclusions to be drawn, and some of the experiments must be repeated with recent improvements in equipment.

The use of surface recombination centers is a general concept, and should be applicable to a number of semiconductor pigments. Therefore, as a first step in examining pigments other than ZnO, we initiated an investigation of rutile. The data suggest that the approach used for ZnO would probably also be successful for rutile.

B. INTRODUCTION

The degradation of thermal control coatings resulting from ultraviolet radiation in vacuum common to many pigments and coating systems containing oxides, e.g., zinc oxide, titanium oxide, and anodized aluminum. We believe the degradation mechanism in most of these systems involves the absorption of ultraviolet light by the semiconductor pigment, followed by capture of the photoproduct holes by surface oxygen, resulting in a higher oxidation state of the oxygen. In vacuum this "active oxygen" is presumably released as a gas and the result will be an excess of metal at the surface of the oxide. This buildup of excess metallic component at the surface is associated in some way with the changes in optical absorption that are associated with a degraded coating.

The requirement for a resistant coating can then be stated simply: Recombination centers must be provided for recombination of photoproduct holes with electrons before chemical effects can occur. If the photoproduct holes are destroyed through a recombination mechanism involving no net chemical change, there is no possibility of coloration.

The above discussion is based on properties of zinc oxide that are well known in semiconductor physics and catalytic surface chemistry. The wavelengths of light responsible for the degradation of ZnO are those having an energy greater than the energy of band-gap edge. In semiconductors, light of band-gap energies produces holes and electrons as the direct process, and does not directly produce any chemical changes. It is known¹ that holes (produced by the light) will cause chemical changes when they get to the clean ZnO surface. Thus we must recombine the holes

before they can effect any chemical damage, and additives which will do so efficiently should solve the problem of ultraviolet degradation.

In this report we discuss the results of research designed to discover good surface recombination centers for ZnO. In Section C the behavior of various chemicals with respect to electron capture and hole capture is examined. Knowledge of these two processes should provide information leading to promising additives, and an understanding of the processes should permit prediction of optimum additives.

In Section D, the testing of the additives exposed to ultraviolet radiation in vacuum is discussed and results presented.

In Section E, measurements designed to elucidate the mechanism of degradation of additive-free ZnO is presented, and theoretical considerations discussed.

In Section F, the possible use of surface recombination centers in other pigments is examined, with rutile being the preliminary test material.

C. INTERACTIONS OF CARRIERS WITH ADSORBED SPECIES

1. Method

In the course of early measurements^{1,2} in which ZnO was studied as a catalyst, we developed methods for studying the electron reactivity and the hole reactivity of chemical species in an aqueous solution. These reactivity parameters are precisely those that are needed to determine the best chemical additive for use as a recombination center. The required reactions are



where M is an active adsorbed chemical in some arbitrary oxidation (valence) state, and M^+ is the species in a higher oxidation state. If the

reaction constants k_1 and k_2 are both high, the chemical couple M/M^+ will be a good recombination center.

Reactions between carriers and additives can also be expressed in terms of electron capture (or hole capture) cross sections, σ . The two expressions are substantially equivalent, with $k = \sigma \bar{c}$, where \bar{c} is the average carrier velocity, of the order of 10^7 cm/sec.

The apparatus used to determine electron and hole reactivity is shown schematically in Fig. 1. From electrical capacity, current, and voltage measurements, it is possible to measure the capture of electrons and/or holes by added chemicals. Since ZnO is negative (cathodic) in the dark, and has essentially no holes, electrons flow to the surface* and undergo a reaction of the type given by reaction (1). When the ZnO is illuminated with ultraviolet light, it is positive (anodic), holes are produced, and the holes flow to the surface* and undergo reaction (2).

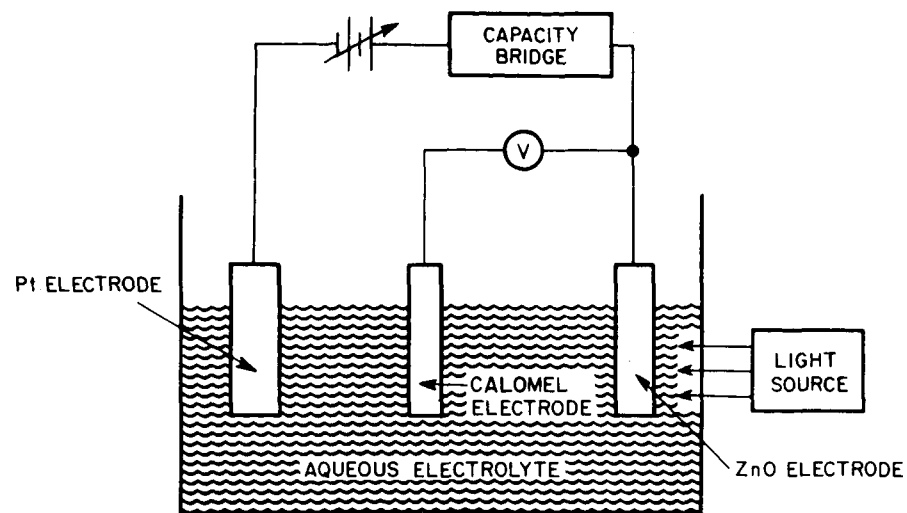
2. Electron Capture Determination

Through the capacity measurement we determine the electron reactivity of M^+ . A high efficiency (high k_1 or σ in reaction 1) is a requisite for good recombination activity. The basis of the determination is the limitation of the current flow in the ZnO system by the surface barrier V_s (the electronic potential difference between the bulk and surface of a semiconductor). The current J is given by the expression

$$J = \bar{c}[M^+] \cdot \sigma_e \cdot \exp(-eV_s/kT) \quad (3)$$

where $[M^+]$ is the density of surface states (associated with substance M^+ available to the electrons, \bar{c} the mean thermal velocity of electrons and σ_e is the capture cross section of the states. The determination of the surface barrier by measurement of the capacity is well established.³ Thus if J is kept constant, the capacity yields the relative values of $[M^+] \cdot \sigma_e$ as we add various substances M^+ to the surface. By

* It has been demonstrated that injection of holes and electrons into the crystal from the solution does not usually occur with most chemicals.



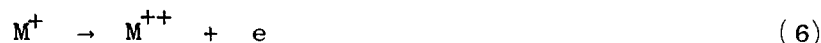
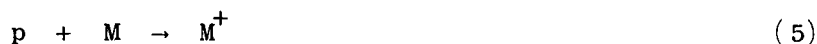
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FIG. 1 ELECTROCHEMICAL APPARATUS

determining the amount sorbed, $[M^+]$, we calculate σ_e ; however, the product $[M^+] \cdot \sigma_e$ is more significant, since it indicates the efficiency of electron capture, that is, the electron reactivity of M^+ .

3. Hole Capture Determination

The occurrence of "current doubling" is used to determine the hole capture of the reduced form of recombination centers. The method can be used as a direct measure of reactions such as (2), the first step in recombination through reducing agents. The phenomenon which we term "current doubling" is based on the observation that some two-equivalent reducing agents follow a series of reactions



Thus under illumination an anodic current becomes doubled,* because each photoproduced hole arriving at the surface leads to the injection of an electron through reaction (6). Hence, hole capture by two-equivalent reducing agents is immediately detected.

The technique was also used to study one-equivalent reducing agents with a large hole capture cross section, such as hexacyanoferrate(II). If the one-equivalent reducing agent has a large cross section, it will capture the hole in preference to a two-equivalent agent also present, and the current will return to normal. Conversely, for a one-equivalent reducing agent M on the surface, we can obtain its efficiency for hole capture by adding BH_4^- (a typical current doubling agent); when enough BH_4^- is present, the holes will go to the BH_4^- instead of to M, and the current will double.

For our recombination centers, substances are needed which do not exhibit current doubling (to avoid net chemical changes), and the above procedures immediately allow comparison of the efficiency of the various

* With no added reducing agents, the current in steady state is equal to the rate of hole arrival at the surface due to the illumination.

candidates for reaction (2). If we wish to evaluate candidates for our recombination centers, we simply determine how much BH_4^- is necessary so that the holes will go to the BH_4^- (causing a current increase) rather than to the recombination center. The more BH_4^- necessary, the better the material is for reaction (2).

4. Results

The relative electron and hole reactivities of various couples are shown in Table I. Both reactivities should be high for a good recombination center. The lower oxidation state of the species in solution was used to obtain the hole capture rate, which is equal to the product of the hole-capture cross section and the sorption constant for the species divided by that for Fe(II). The higher oxidation state of the species in solution was used to obtain the electron capture rate which is equal to the product of electron-capture cross section and the concentration of the sorbed species corresponding to an aqueous solution concentration of 0.01 M.

Table I

System	Hole Capture Rate Relative to Fe(II)	Electron Capture Rate 0.01 M Solution
Arsenic III/V	0.1	0
Copper I/II	~ 1	~ 0
Sodium Tartarate	--	3×10^{-11}
Iodine O/I	3	10^{-10}
Chromium III	--	10^{-9}
Iron (ferro/ferricyanide)	1	10^{-8}
Iron III (chloride)	--	10^{-7}
Manganese VII	--	1.6×10^{-4}

It is observed that the hole capture rate has a rather modest variation with the materials studied. Since these measurements were made, Gomes^{2b} has made a more detailed study of the hole capture cross section

of some reducing agents of chemical interest. Using the hole capture rate for iodine given in Table I to normalize the data, we can list his results for the hole capture rate relative to Fe(II):

SO_3^{2-}	1
Br^-	.05
CH_3OH	.3
$\text{C}_2\text{H}_5\text{OH}$.5
Cl^-	~ 0

There is a significant variation between hole capture rates of the different species, but it is not clear at present how much of this variation should be attributed to variation in sorption constant. The systematic variation through the halogens is of interest, however.

The electron reactivity of the oxidized form shows a wider spread. The lower limit of our rate measurement was about 2×10^{-11} , so the value for tartarate probably has no significance. The values for Cr(III) and Mn(VII) are approximate, as the $\log \text{current}/(\text{capacity})^{-2}$ curves did not follow Eq. (3), but showed a slope closer to $kT/2e$ or $kT/3e$.

One of the important aspects of this type of data is a detailed measure of the expected recombination efficiency of various candidates. Thus Table 1 indicates that Fe and Mn are potentially good recombination centers.

These data also provide background for a model permitting prediction of the best additives. Thus we have developed a tentative interpretation of the electron reactivity of the oxidized form of the materials studied. In the process of interpretation we have been aided substantially by preliminary results obtained in our basic study¹ of the energy of surface states at the ZnO surface.

As a first approximation we have found it instructive to compare the results of the electron reactivity and the surface state energy measurements with the conventional standard oxidation-reduction potentials.⁵ In Fig. 2, we have plotted values of electron-capture efficiency expressed as $\sigma[X]$ (the product of the cross section of the species and

the adsorbate density, as reported in earlier progress reports for 10^{-2} molar solution) against the oxidation-reduction potential for each species. In Fig. 3, the surface energy levels E relative to the conduction band are plotted as a function of the standard oxidation-reduction potential for several species. Here the identification of the $O^=$ species is not conclusive.

From these sparse data one can tentatively draw some correlations between the electron reactivity, the surface energy level, and the oxidation-reduction potential of the various species.

It is observed, for example, that at an oxidation-reduction potential of about -0.4 volt, both the activation energy E and the product $\sigma[X]$ seem to approach zero. We are therefore tempted to suggest that this value of the oxidation-reduction potential corresponds more or less to the energy of the bottom of the conduction band. Materials of oxidation potentials more positive than -0.4 volt could then be expected to have energy levels above the bottom of the conduction band, and thus be unable to capture electrons.

Materials with more negative than -0.4 volt can be separated into two groups; the behavior of one can be simply interpreted, the other is more complex. In the first group, simple theory of electron capture, involving the emission of a phonon, could predict the maximum sketched in Fig. 2. Thus the behavior of this group of materials can be tentatively explained. However, the subsequent rise in $\sigma[X]$ for Cr and Mn is harder to explain. It was originally considered that this latter group may have levels deep enough to cause hole injection. However, an attempted test of this prediction for permanganate yielded no support for the idea. Two types of tests were made. The first was based on the consideration that if holes are injected, hole trapping should be observed. The trapping is detected by an apparent increase in donor density and occurs with holes produced, for example, by ultraviolet. Negligible increase was observed under conditions where permanganate should be injecting. Second, if holes are injected, the ZnO should fluoresce as observed when holes are produced with ultraviolet illumination. Fluorescence was not observed.

With hole injection tentatively rejected as the reason for the rise in electron reactivity for high negative oxidation potentials, other possibilities must be considered. One such possibility is the oxidation (electron removal) by the permanganate of surface states which otherwise would be occupied. However, a good test for the validity of this hypothesis has not been conceived.

Our tentative working model for the recombination efficiency can be summarized as follows. We interpret the above measurements and theory as indicating that one-equivalent materials with a surface state a few tenths of an electron volt below the ZnO conduction band will be ideal. Something is suspect about the behavior of the strong oxidizing agents, such as Cr(III) and Mn(VII), which do not follow the simple electron capture formula, Eq. (3), and do not follow the expected cross section relationship referred to in Fig. 2. A reaction with a surface state may be occurring, and if the surface state is an oxygen species, the additive may be detrimental rather than beneficial in reducing degradation.

Further work on other materials with oxidation-reduction potentials in the neighborhood of -0.7 are obviously needed to test the theoretical predictions and to discover other promising candidates.

However, of the materials studied, iron appears to be the most promising additive, and therefore the tests on the ZnO-vacuum interface were initiated with iron as the test recombination center.

D. TESTS OF RECOMBINATION EFFICIENCY AT THE ULTRAVIOLET/VACUUM INTERFACE

After determining from the above detailed studies which materials looked promising as recombination centers, the next step is to make a more realistic test of efficiency. We needed a test to show whether the additives indeed prevent permanent changes of the properties of ZnO in vacuum under ultraviolet light. However, a test was required that was simpler to do and to interpret than the complex optical degradation tests.

The test method initially considered for the ZnO-vacuum evaluation of additives involved measurements of gas evolution; it was ruled out because gas evolution did not occur. However, this method and the information obtained are pertinent to the mechanism of photodegradation of additive-free ZnO, and will therefore be discussed under that section.

Recently two alternate methods have been examined: DC electrical conductivity^{3,4} and electron spin resonance (ESR). The DC conductivity method is particularly suitable for single crystals. It consists of measuring the change of the dark conductivity due to photoirradiation; such a change reflects a change in the concentration of conduction band electrons in the bulk. The ESR method, particularly applicable to powders, consists of measurements of two types of signals that are expected to change upon photoirradiation. The first, at $g = 1.96$, is a measure of the conduction band electronics; the second, at $g > 2$, is a measure of surface lattice oxygen that has been oxidized by photoproduced holes.

1. Conductivity Measurements

A lithium-doped crystal of ZnO, obtained from Minnesota Mining and Manufacturing Company, was used. Lithium increases the resistivity and thus in these experiments improves the sensitivity. Results with no additive were substantially the same as those of Collins and Thomas, indicating a permanent increase in conductivity due to exposure of the sample at a pressure of 10^{-6} mm Hg to band gap illumination from a tungsten lamp. A four-point resistance measurement was used, with indium contacts. Measurements were also made on a sample dipped in an aqueous solution containing 0.01 M $K_3Fe(CN)_6$ and 0.01 M $K_4Fe(CN)_6$. After dipping, the excess moisture was soaked off, then the sample was dried in air under an infrared lamp for 10 minutes. No detectable permanent conductance change was produced by irradiation in the presence of the additive under the same conditions as above.

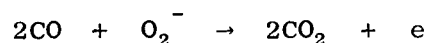
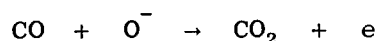
These results are preliminary but, if confirmed, they will be an important verification of the concepts discussed in this report.

2. ESR Measurements

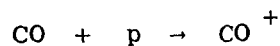
The ZnO (New Jersey Union Company grade SP 500) was introduced into a flat cell with inner dimensions of 1 mm x 8 mm x 30 mm. This geometry provides optimum access to photoirradiation during ESR measurements. The ZnO was pretreated by heating at 500°C in vacuum for 1 hour. The ESR measurement was made after various treatments. In addition, the crystal current (CC) was recorded. CC is a measure of the microwave bridge unbalance, which depends upon the electrical conductivity of the ZnO.

Photoirradiation of the pretreated ZnO resulted in several changes of ESR parameters. A rapidly reversible change in CC occurred, which indicates an increase in the number of photoproduced conduction electrons. A corresponding increase in the 1.96-line occurred, but the effect was small. A permanent change in CC and the 1.96 line occurred, which indicates photodesorption of oxygen (especially when small amounts of oxygen had been intentionally sorbed) and also photoproduction of donors. A 2.02 line appeared, and this may be due to the formation of a hole type defect, i.e., because the g value > 2 . Even with an infrared optical filter, some thermal heating was noted, and this, of course, caused some increase in conductivity.

Some experiments with CO sorption after photoirradiation were performed to determine whether the presence of photoproduced sorbed oxygen, e.g., O^- or O_2^- , could be detected by reactions such as:



An increase of conductivity occurred, but the effect was also observed for unirradiated ZnO left standing the same length of time. It is therefore not possible at this time to distinguish between sorbed oxygen resulting from photoirradiation and from transfer from the glass walls. The CO sorption also caused the 2.02 line to disappear. This may have occurred by a reaction of the type:



where p represents a positively charged center associated with the 2.02-line.

These preliminary results indicate that the ESR approach may be useful for studying photodegradation by correlating the changes of the 2.02-line with color changes, and by determining the photoproduced hole-electron pair recombination rates as affected by photodamage or intentional doping. The latter determination may possibly be made on powders by recording the rate of change of conductivity upon irradiation.

E. OPTICAL DEGRADATION OF UNTREATED ZnO

To date no firm conclusions have been reached on the detailed mechanism of optical degradation (yellowing) of untreated ZnO in ultraviolet light under vacuum. Below we describe several measurements which may help to understand the process, and present our current working hypothesis for the effect. Mass spectrometer measurements, apparently indicating no oxygen evolution, raise questions about information deduced from conductivity measurement³ as to the chemical reactions of holes at the surface. Measurements show similar optical absorption characteristics for ZnO with dislocations and for photodegraded ZnO. Electrical measurements on photodegraded crystals tentatively indicate the same characteristics as observed with dislocations. The model we propose as a working hypothesis is that dislocations are directly responsible for the anomalous optical absorption, and that many causes of degradation each produce a deformed ZnO powder as the common end product.

1. Photolysis of ZnO (Mass Spectrometer Measurements)

It has been concluded by several workers^{3,4} that photodesorption of oxygen from ZnO should result from ultraviolet illumination. Experiments to observe this have been carried out both to establish this step in the degradation process and to serve as a measure of improvement by recombination centers. No observable photodesorption was observed. The experimental conditions and the possible reasons are described below.

Investigations of the photodesorption products during photolysis by ultraviolet light were performed for samples having various pre-exposure treatments. Product analysis was made with the mass spectrometer modified to respond to a greater mass range (to mass 80), and with greater sensitivity than previously.

Zinc oxide single crystals prepared in three different ways were each irradiated with two different mercury arc sources. One sample was etched in nitric acid for a short period before being rinsed, dried, and placed in the vacuum chamber; a second sample was lapped, then etched in concentrated phosphoric acid; the third was etched in phosphoric acid, then lapped before introduction into the vacuum chamber. All samples were subjected to an overnight 250°C bakeout before they were exposed to light. The two light sources were the 100-watt General Electric A-4 lamp, previously used, and the 200-watt PEK Labs 200-2 lamp mounted in a Bausch and Lomb housing equipped with a condenser lens. (The vacuum chamber used for the analysis of photodesorption products was equipped with Pyrex windows so that the shorter wavelength portion of the quartz lamp was not transmitted). The experiments were conducted under the "pump-out mode" conditions.

The observed partial pressures of O_2 ($M/e = 32$) and O ($M/e = 16$) remained essentially the same during exposure to the ultraviolet light as before exposure. This pressure was of the order of 10^{-10} torr for mass 32 (oxygen). The background ion current was much higher for mass 16, which makes it difficult to analyze for oxygen atoms in the system. (The ion current for mass 16 is believed to be limited by the mass spectrometer proper.) Slight increases in partial pressures for carbon monoxide and carbon dioxide were noted upon exposure of the samples to light. Similar increases were noted in blank experiments in which an equivalent portion of the Pyrex chamber walls alone were irradiated, indicating that probably most of the gases evolved during irradiation are coming from the walls. A series of experiments were conducted with the nitric acid-treated ZnO samples exposed to a high pressure of oxygen (10^{-1} torr) for 4 hours immediately before irradiation by ultraviolet light. Under these conditions the dark steady-state pressure was high

($\sim 10^{-6}$ torr), and a larger desorption rate for carbon monoxide, carbon dioxide, and water was observed. Experiments were also performed with the phosphoric acid-treated samples after they had been heated to 200°C under 10^{-7} torr vacuum for 4 hours immediately before exposure to light. The results were similar to those for the samples that were exposed to bakeout before exposure to light. No masses in the range 44-80 were observed above partial pressures about 10^{-11} torr, the present sensitivity of the instrument.

The purpose of the experiment with lapped samples was to check the hypothesis that excess Zn atoms near the ZnO surface are acting as recombination centers, and that decreasing their concentration during irradiation would decrease recombination rate and thus increase reaction of the holes with surface oxygen. We assume that the zinc atoms formed by photoirradiation diffuse to dislocation centers and precipitate there; thus dislocations introduced by lapping should enable more rapid precipitation and a greater oxygen evolution rate. However, for the lapped ZnO, as for the etched ZnO, no oxygen evolution was observed, contrary to expectations based on present theory. The lack of experimental evidence for photodesorbed oxygen may be due to (a) our inability to detect the desorbed species with the present apparatus (if O atoms are desorbed, they may stick to the walls), (b) very high hole-electron recombination rate, or (c) retention of neutral oxygen on the surface of the ZnO (perhaps reacting with surface contaminants).

2. Effect of Dislocations on Optical Absorption

In order to prepare a crystal with a minimum of surface dislocations and with good optical faces (to avoid surface light scattering), chemical etching and polishing techniques have been developed. Mechanical polishing techniques cannot be used to reduce surface scattering because they may introduce dislocations. We found that dilute aqueous acids, especially HCl, will etch the (0001) face, and 85% H_3PO_4 will polish this face; the reverse was found for the other crystal face, (000 $\bar{1}$). With these etches available, flat chemically polished ZnO could be prepared for a substantially dislocation-free reference.

A series of optical transmission experiments in air showed that the band edge of ZnO shifted toward the visible when dislocations were introduced on either face of the crystal. The band-edge shift was visible to the naked eye--the crystals became yellow. That the yellowing was a surface effect was shown by its removal by chemical etching. The effect was indistinguishable from the photodegradation shift.

3. Electrical Effects Associated with Optical Degradation

Spectrophotometer studies were made of a single crystal exposed to ultraviolet in vacuum for 300 hours, using as a light source a PEK 200-watt lamp. The system consisted of a quartz collimating lens (Bausch and Lomb monochromator light housing) and quartz windows ("supersil") in the vacuum system, which was operated at a pressure of 10^{-8} to 10^{-9} torr. Changes did occur in the crystal, since a slight browning was visible to the eye. However, the spectrophotometer was not sensitive enough to distinguish these changes clearly, and so it will have to be modified.

Electrical measurements of the degraded sample were made to examine the electrical properties of the flaws associated with the degradation. In preliminary measurements it was observed that the side exposed to the ultraviolet showed a very short bulk lifetime near the surface, indicating that the flaws induced by the ultraviolet act as bulk recombination centers. Hole trapping at the flaws was also evident.

It should be noted that dislocations provide the same electrical behavior as that noted above. However, flaws other than dislocations could exhibit this behavior. Following the completion of the electrical measurements, an etch pit count of dislocations was made to see if the density had increased. These measurements did not yield clear results and further studies are necessary.

4. Theoretical Considerations

The possible cause for ultraviolet vacuum optical degradation of ZnO has been considered in order to establish the experimental approach to be used. Without a working hypothesis, it becomes difficult to devise critical experiments.

It is clear from all evidence of semiconductor/photon interactions that the primary effect of the photon is to produce electron-hole pairs. It would appear from the work of Lander² that the secondary effect is the photolysis of ZnO, leading to evolution of oxygen with the reduced zinc retained on the ZnO. One would then be tempted to say that the diffusion of zinc into the crystal would (a) result in the infrared absorption due to the free electrons and (b) result in extra ultraviolet absorption, perhaps associated with the interstitial zinc.

However, one major factor suggests that this simple explanation cannot account for the observed ultraviolet absorption: Lander⁶ observed that the solubility of excess zinc at room temperature in ZnO is extremely low (about $2 \times 10^9 \text{ cm}^{-3}$). This low zinc concentration is unlikely to account for the strong optical effects observed.

A more likely explanation is that the excess zinc precipitates at dislocations, rather than dissolving in the bulk material. Thus, the slow process in the degradation of the pigment is the "distillation" of excess zinc from the surface of the ZnO to dislocations in the material.

Lander⁶ showed that precipitation of lithium at dislocations in ZnO occurs, and will occur to such an extent that the crystal can be strained; in fact this author talks about the ZnO "disintegrating" due to precipitation during cooling.

Thus a tentative mechanism is:

- (a) Photolysis produces excess zinc at the surface. When the order of 10^{14} or 10^{15} excess zinc/cm² is developed, the material is so n-type that further photolysis is stopped by direct electron-hole recombination. A steady state is reached under illumination so that as zinc diffuses into the interior, it is replaced through further photolysis.
- (b) Zinc "distills" from the surface to dislocations. The precipitation of zinc causes stresses in the lattice, producing more dislocations.

- (c) As the concentration of dislocations increases, the strained crystal absorbs in the ultraviolet; i.e., the absorption edge develops a tail. An alternate but less attractive model is that the precipitated zinc on the dislocations absorbs in the ultraviolet, so the color center is a zinc-dislocation complex.

Some direct evidence for this model (that the optical absorption is associated with the dislocations) arises from the observed discoloration of intentionally strained ZnO. Strained ZnO has a yellow cast similar to the appearance of degraded ZnO. Further evidence that this model is feasible arises from the work of Hsu⁷ and coworkers, who found in GaAs that severe damage to a crystal caused a tail on the absorption edge (which could be construed as a peak near the absorption edge if one subtracts the normal absorption), looking much like the excess absorption in ZnO. These workers used a high intensity neutron flux to disorder their crystals, illustrating the possible connection in our problem between the photolysis-produced ZnO absorption edge tail and the tail produced by high energy irradiation of ZnO.

With this mechanism in mind, some of our preliminary optical measurements have been a comparison of the optical absorption of ultraviolet-vacuum degraded ZnO and strained ZnO.

F. PRELIMINARY MEASUREMENTS ON RUTILE

Fundamental studies on single crystal rutile (TiO_2) were initiated for the purpose of developing a capability to investigate a thermal control pigment other than ZnO. These studies consisted of investigating the feasibility of adapting our ZnO techniques to rutile and can be divided into: (a) etching and polishing, (b) adjustment of donor density by chemical treatment, (c) measurement of the donor density near the surface by the electrolytic voltage-capacitance method, (d) cathodic reduction processes, and (e) photo and dark anodic oxidation processes. All studies were made on the (001) crystallographic face.

Molten KOH (400-500°C) slowly (30 min) removes scratch marks, while boiling 100% H_2SO_4 does not seem to etch TiO_2 . The ability to control dislocations densities was expected to be important, since we believe that dislocations may play an important role in the degradation of thermal control coatings. In addition, it is possible for dislocations to dominate our electrical measurements.

We utilized the known fact that the donor density can be adjusted by reduction with H_2 or oxidation by O_2 at elevated temperatures. There was a difference in the color of rutile resulting from a 30-min reduction in 1 atm of flowing H_2 at 400°C, depending on whether the sample had been previously etched. Non-etched samples turned grey, while two etched samples remained white. These observations supported our notion, developed for ZnO , that dislocations are intimately connected with the degradative coloration of thermal control coatings. Presumably the greying resulted from the multiplication of dislocations accompanying the chemical reduction procedure. Our theory assumes that the photolysis in vacuum results in oxygen loss which is also a reduction procedure.

The donor density near the surface was measured by the electrolytic voltage-capacitance method. On non-etched samples, low conductivity preparations showed no voltage dependence for the capacitance, while high conductivity preparations did show a voltage dependence, but the values of the capacitance were high. When the capacitance values are high it is possible that they are not associated with the depletion region of the semiconductor but with the Helmholtz capacitance. Thus high capacitance measurements are not reliable. Interpretable results were obtained on an etched sample, reduced for 30 min in H_2 at 400°C. The voltage dependence of the capacitance indicated a donor density of about 10^{17} cm^{-3} . These preliminary results suggest that the apparent value of the donor density is reasonably stable near the surface in contact with an aqueous solution, but that the Helmholtz voltage changes. We did not determine the cause of the instability.

Cathodic reduction of oxygen was observed by the difference in current between a solution saturated at 1 atm with O_2 versus one de-aired

by N_2 . We have no indication whether the reduction mechanism is electron capture or hole injection.

Anodic processes on the (001) face of rutile and on the (0001) face of ZnO have some differences and some similarities. First, while the anodic dark currents are higher on rutile, they are similar to those on ZnO in that the dark current is unaffected by methanol, ethanol, or formate ion from pH 4 to 12.5. On the other hand, the photo current of rutile is also unaffected by these chemicals with or without O_2 , in contrast to results on the (0001) face of ZnO. We have not determined the chemical oxidation process caused by the reaction of holes photogenerated within rutile.

These preliminary results indicate that electron capture by additives should be measurable (as was observed with oxygen), but new methods may be required for hole capture measurement. However, with ZnO the latter seemed the least critical of the measurements, so the results indicate that our ZnO approach should be applicable to rutile in all important phases.

G. CONTINUING STUDIES

We plan to continue the studies with no major changes in direction. Research aimed at the identification of additives for surface recombination centers will be continued to find other materials and better materials than iron. The conductance method and the ESR method of testing the effectiveness of these centers will be developed further. They will be used both to test additives suggested by the electrolyte studies and to find optimum methods of application of additives to practical pigments.

Further studies of the electrical and chemical properties of additive-free ZnO will be made, to clarify the nature of the centers.

Use of the approach or a pigment other than ZnO will be continued; the pigment still is to be selected.

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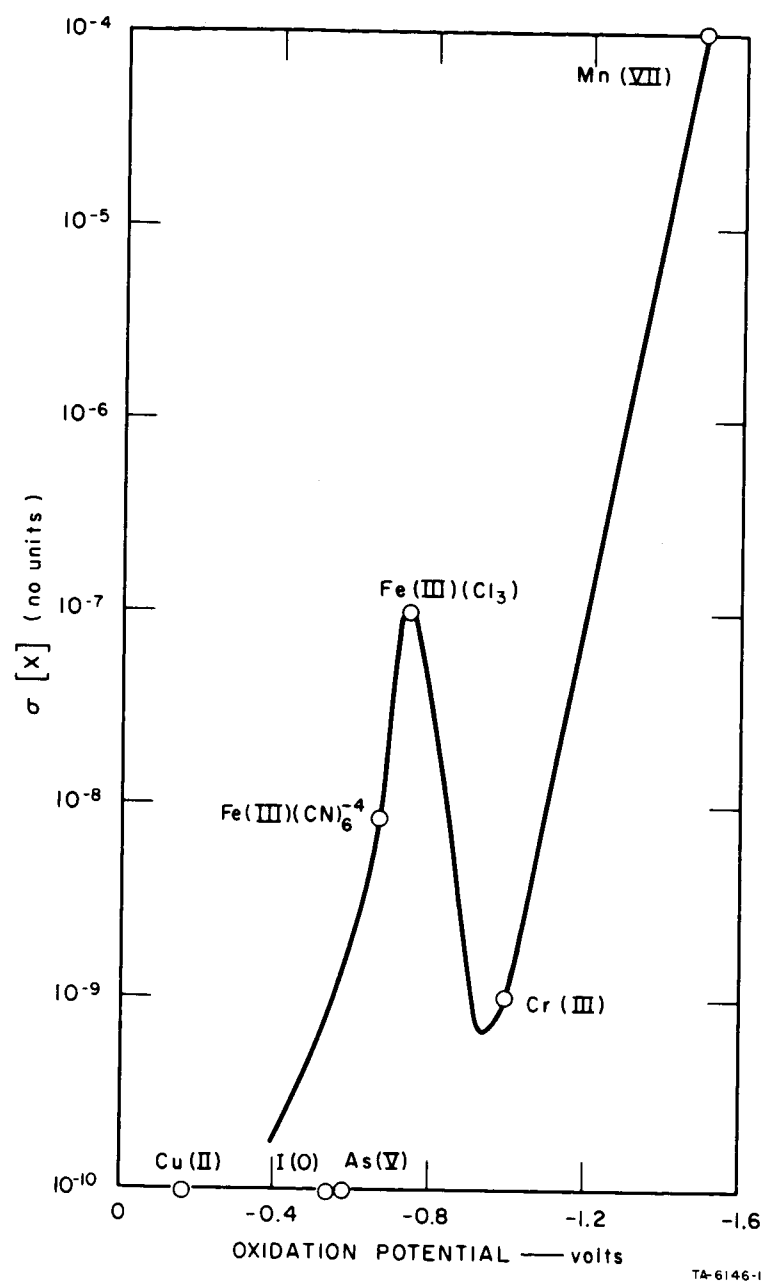


FIG. 2 ELECTRON REACTIVITY OF VARIOUS CHEMICALS (REDUCED FORM) AS A FUNCTION OF OXIDATION-REDUCTION POTENTIAL

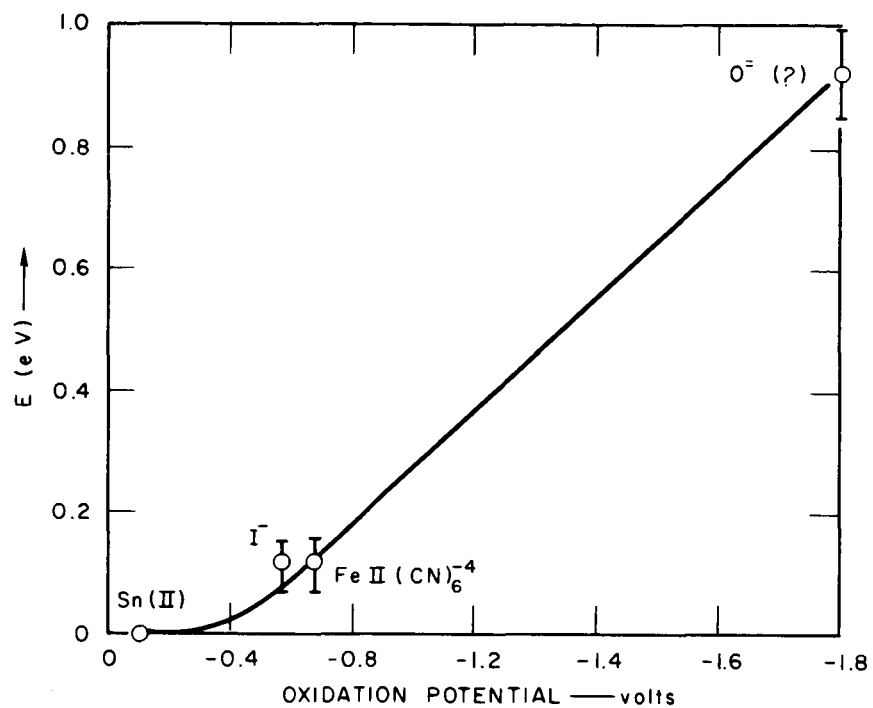


FIG. 3 SURFACE STATE ENERGY E OF VARIOUS CHEMICALS (OXIDIZED FORM) AS A FUNCTION OF OXIDATION-REDUCTION POTENTIAL